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On the microscopic origin of chemical short-range order in transition metal glasses

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Abstract. We present microscopic calculations of the chemical short-range order in amorphous alloys of two transition metals. Our approach is based on a model tight-binding Hamiltonian and a thermodynamic variational approach founded on the Gibbs–Bogolyubov inequality and a hard-sphere Yukawa fluid as a reference system. The manifestation of chemical short-range order (CSRO) in structural properties is investigated. Its effect on the stability of transition metal amorphous alloys is also discussed in terms of heats of formation. The occurrence of CSRO is then discussed in correlation with the electronic structure of these alloys. Using the Hellmann–Feynman theorem we show that the ordering energy that creates CSRO has two contributions. The first one is kinetic and is due to the modification of the density of the electronic states with CSRO. It is equivalent to the term which is classically calculated in the TB CPA GPM for which the atomic energy levels are independent of CSRO. The second contribution is an electrostatic one but is weaker than the first one due to the small charge transfer in those systems. We explain how CSRO is favoured when the Fermi level falls in a bonding states range created by the coupling between the states of the alloying partners.

1. Introduction

Since all the metallic glasses which are stable at room temperature are alloys, the state of mixture of the alloy components is an important parameter of the system. Very recent structural investigations have shown that, in fact, a completely random mixture is not attained, so that the chemical composition around the atoms of each alloying component is different from the average. For instance, the results for $\text{Ni}_{40}\text{Ti}_{60}$ [1] and $\text{Ni}_x\text{Zr}_{1-x}$ ($x = 0.35, 0.5, 0.65$) [2–4] as well as for $\text{Ni}_{33}\text{Y}_{65}$ [5] and $\text{Ni}_x\text{Nb}_{1-x}$ ($x = 0.36, 0.62$) [6, 7] show a degree of chemical ordering (CSRO) which can vary either with the composition as in the case of $\text{Ni}_x\text{Zr}_{1-x}$ or $\text{Ni}_x\text{Nb}_{1-x}$ system or with the partner species as in the $\text{Ni}_x\text{M}_{1-x}$ series ($M = \text{Ti}, \text{Zr}, \text{Y}, \text{Nb}$). Unfortunately, experimental determinations of chemical ordering are not sufficient to get a complete understanding of this phenomenon and a microscopic theory of CSRO would be welcome. The widely used theory for studying electronic properties of substitutional disordered transition metal alloys is the coherent potential approximation (CPA). However in spite of its many desirable properties, the CPA is a single-site theory that cannot treat effects such as CSRO. Some significant advances of the general theory of substitutional disordered alloys have been made to

take into account CSRO. For example Gautier and co-workers [8] have proposed a generalised perturbation expansion about the energy of the random alloy calculated in CPA from which pair and cluster interactions are obtained. Robbins and Falicov [9] have also proposed to include CSRO explicitly in the calculation of the electronic spectrum of substitutional transition metal alloys, using the cluster Bethe lattice method. In the same way, a qualitative and quantitative description of CSRO has been proposed [10–11] for topologically disordered alloys, like amorphous or liquid alloys. In this approach, two distinct steps are required: (i) the determination of the concentration dependence of electronic properties like internal energy from a model tight-binding Hamiltonian [12] and (ii) the calculation therefrom of the structural and thermodynamic properties using a thermodynamic variational technique found on the Gibbs–Bogolyubov inequality and a hard-sphere Yukawa fluid as a reference system [13, 10]. More particularly, our method allows us to take into account CSRO and to show its effect on the properties of the amorphous alloys. Of course, the thermodynamic variational approach is strictly applicable only to liquid systems but for amorphous alloys, we will have to assume that their CSRO is essentially identical to that of a supercooled liquid alloy just above the glass transition temperature.

In a first paper, [11] (hereafter referred as I) results concerning structural information about $\text{Ni}_{40}\text{Ti}_{60}$ and $\text{Ni}_x\text{Zr}_{1-x}$ amorphous alloys have been reported, showing that calculated and experimental Bhatia–Thornton partial structure factors are in good agreement. In the first part of this paper, we complete our structural determinations for other amorphous alloys for which experimental results are available. We also focus our attention on the thermodynamic excess functions that will allow us to discuss the stability of these phases. More particularly, we compare the calculated heats of formation with the available experimental ones. In the second part, all these results are thus used as a starting point to discuss the evolution of chemical ordering as a function of the alloying partners. The role of the traditional alloy chemical factors, chemical bonding and valence electron concentration, in establishing CSRO is presented: more particularly, we try to analyse qualitatively the microscopic origin of the ordering energy that creates CSRO. Using the Hellmann–Feynman theorem we show that the ordering energy that creates CSRO has two contributions. The first one is kinetic and is due to the modification of the density of the electronic states with CSRO. It is equivalent to the term which is classically calculated in the TB CPA GPM for which the atomic energy levels are independent of CSRO. The second contribution is an electrostatic one but is weaker than the first due to the small charge transfer in those systems. We explain how CSRO is favoured when the Fermi level falls in a bonding states range created by the coupling between the states of the alloying partner.

The paper is organised as follows: in § 2 we present briefly the calculation of the electronic ground-state energy and the properties of the reference system. We present an application of our method to $\text{Ni}_x\text{Zr}_{1-x}$ and $\text{Ni}_x\text{TM}_{1-x}$ (TM = Ti, Y, Nb) amorphous alloys in § 3. In § 4 the microscopic origin of CSRO is discussed.

2. Model

In order to calculate the electronic ground-state energy of an alloy one can express the free energy as a function of the atomic coordinates, the equilibrium configuration is thus obtained by minimisation of the free energy. As total energies are easily calculated in a tight-binding approximation, this approach appears to be attractive for transition metal

alloys. However a straightforward minimisation of the free energy with respect to the atomic coordinates is, of course, out of the question. On the other hand, we might parametrise the structure in a simple way and minimise the free energy with respect to a small number of relevant parameters. This is precisely what is done in a thermodynamic variational technique based on the Gibbs–Bogolyubov inequality. According to this approach, the equilibrium configuration is thus calculated by minimising the variational expression [10]:

$$F(p_i, p_j, \dots) = 3/2 k_B T + E_T(p_i, p_j, \dots) - TS_{\text{ref}}(p_i, p_j, \dots) \quad (2.1)$$

and the variational conditions are:

$$\frac{\partial F}{\partial p_k}(p_i, p_j, \dots) = 0 \quad \text{for all } p_k, \quad (2.2)$$

$p_i, p_j, \dots, p_k, \dots$ being the parameters modelling the reference system; $S_{\text{ref}}(p_i, p_j, \dots)$ is the entropy of the reference system.

At the level of a thermodynamic variational calculation, the crucial step is the selection of an appropriate reference system. For alloys with a nearly ideal mixing behaviour, a variational treatment with a mixture of hard spheres of different diameters as a reference system has met with considerable success [13, 14] but such an approach is certainly unable to cope with ordering phenomena. Copestake *et al* [15, 16] have shown that the structural manifestations of ordering in molten salts, liquid semiconductors and even in liquid metallic alloys may be modelled by a mixture of hard spheres having all the same diameter but opposite charges (however respecting the overall charge neutrality condition) and interacting through a Coulomb or screened Coulomb (Yukawa) potential. In this system, the description of the atomic configuration requires three parameters which are the diameter of the hard sphere σ , the strength of the ordering potential at hard contact ε and a screening constant K . For such a reference system, an analytical solution of the mean spherical approximation is available [17] and very recently Pasturel *et al* [18] have shown that a thermodynamic variational approach to chemical short-range order may be based upon this reference system. In terms of the average and ordering potentials, the reference interactions are given by:

$$\varphi_{\text{NN}}(r) = \begin{cases} \infty & r < \sigma \\ 0 & r > \sigma \end{cases} \quad (2.3a)$$

$$\varphi_{\text{cc}}(r) = \begin{cases} \infty & r < \sigma \\ -\varepsilon \sigma \exp(-K(r - \sigma))/r & r > \sigma \end{cases} \quad (2.3b)$$

$$\varphi_{\text{Nc}}(r) = 0. \quad (2.3c)$$

Because of equation (2.3c) the three coupled integral equations of the mean spherical approximation (MSA) decouple into two independent equations. One with the closure conditions (to the Ornstein–Zernike equations)

$$h_{\text{NN}}(r) = -1 \quad r < \sigma \quad (2.4a)$$

$$c_{\text{NN}}(r) = 0 \quad r > \sigma \quad (2.4b)$$

describes the fluctuations in the mean number density and is identical to the Percus–

Yevick equations for hard spheres, hence we know its analytical solution [19]. The second, with the closure conditions:

$$h_{cc}(r) = 0 \quad r < \sigma \quad (2.5a)$$

$$C_{cc}(r) = \varepsilon \sigma \exp(-K(r - \sigma)/rk_B T) \quad r > \sigma \quad (2.5b)$$

describes the local fluctuations in the compositions. Its analytical solution has been given by Waisman [17]. Within this reference system, the variational conditions given in equation (2.2) become:

$$\begin{aligned} \frac{\partial F}{\partial \sigma}(\sigma, \varepsilon, K)|_{T, n, \varepsilon, K} &= 0 \\ \frac{\partial F}{\partial \varepsilon}(\sigma, \varepsilon, K)|_{T, n, \sigma, K} &= 0 \\ \frac{\partial F}{\partial K}(\sigma, \varepsilon, K)|_{T, n, \sigma, \varepsilon} &= 0 \end{aligned} \quad (2.6)$$

with the variational upper bound to the exact free energy

$$F(\sigma, \varepsilon, K) = 3/2 k_B T + E_T(\sigma, \varepsilon, K) - T(S_{HS}(\sigma) + S_{ord}(\sigma, \varepsilon, K)). \quad (2.7)$$

Explicit expressions for the HS and the ordering contributions to the entropy (S_{HS} and S_{ord}) are given in references [11, 18].

Let us turn back to the calculation of the electronic ground-state energy $E_T(\sigma, \varepsilon, K)$ for a given configuration. The total energy can be written as the sum of two terms, namely:

$$E_r = E_{rep} + E_{bond} \quad (2.8)$$

where the labels imply that the first contribution is repulsive and the second attractive, stemming from the quantum-mechanical bonding between the atoms. As we are interested in the variations of total energy with CSRO, we keep only the E_{bond} contribution in which the interionic Coulomb interactions have been absorbed. Within these conditions, the tight-binding Hartree Hamiltonian used in our calculations can be divided into three terms:

$$H = H_{1e} - H_{ee} + H_{ion-ion} \quad (2.9)$$

where H_{1e} is the one-electron tight-binding Hamiltonian, H_{ee} is the electron–electron interaction (subtracted from the one-electron Hamiltonian since this interaction is counted twice in H_{1e}) and $H_{ion-ion}$ is the interaction between the ions. The one-electron Hamiltonian can still be written as:

$$H_{1e} = \sum_{i\mu} |i\mu\rangle \varepsilon_{i\mu} \langle i\mu| + \sum_{i\mu j\nu} |i\mu\rangle t_{i\mu, j\nu} \langle j\nu| \quad (2.10)$$

where $|i\mu\rangle$ is the ket for the orbital μ at site i (we have employed a minimal tight-binding basis of five d orbitals per atom). In our calculations, we assume that the on-site $\varepsilon_{i\mu}$ and hopping $t_{i\mu, j\nu}$ energies depend only on the species of atom at the relevant sites and in the case of hopping parameters, on the relative positions of the sites.

The internal energy is thus given (as in I) by:

$$\begin{aligned}
 E_T(\sigma, \varepsilon, K) = & \int_{-\infty}^{E_F} EN(E, \sigma, \varepsilon, K) - 1/2 U|x_A n_A^2(\sigma, \varepsilon, K) + x_B n_B^2(\sigma, \varepsilon, K)| \\
 & - 2\pi\rho x_A x_B \{2[\delta n_B(\sigma, \varepsilon, K) - \delta n_A(\sigma, \varepsilon, K)] [n_B(\sigma, \varepsilon, K) - n_A(\sigma, \varepsilon, K)] \\
 & + [\delta n_A(\sigma, \varepsilon, K) - \delta n_B(\sigma, \varepsilon, K)]^2\} \int_0^\infty g_{cc}(r)V(r)r^2 dr \quad (2.11)
 \end{aligned}$$

where U and $V(r)$ describe the intra-atomic and interatomic Coulomb interactions, $\delta n_i = n_i - n_i^0$ the charge transfer on metal i , $g_{cc}(r)$ being the partial pair correlation function of the reference system which represents the given atomic configuration. For interatomic Coulomb interactions, we adopt an interpolation formula $V(r) = e^2/(r + U^{-1}e^2)$ [11].

To calculate the electronic density of states $N(E, \sigma, \varepsilon, K)$, we use a Bethe Lattice type approximation introduced by Mayou *et al.*, [12] which is similar for disordered alloys to the approximation applied by Falicov and coworkers [20] to describe short range order in crystalline alloys. For the d bands, the approximation that we use leads to a degeneracy of the five orbitals; it is due to the isotropy of the mean environment and implies that the five orbitals have the same density of states. We obtained the following equations of coupling between Green's functions of one orbital on A or B component:

$$\begin{aligned}
 G_A(z) &= \frac{1}{z - \varepsilon_A - \mu_{AA}^2 G_A(z) - \mu_{AB}^2 G_B(z)} \\
 G_B(z) &= \frac{1}{z - \varepsilon_B - \mu_{BB}^2 G_B(z) - \mu_{BA}^2 G_A(z)} \quad (2.12)
 \end{aligned}$$

where μ_{AB}^2 is the average of the second moment of hybridisation between the electronic states of the two components. The different μ_{ij}^2 ($i = A$ or B , $j = A$ or B) can be expressed in function of partial pair radial distribution function g_{ij} [12]:

$$\mu_{ij}^2 = \rho \int_{-\infty}^{\infty} t_{ij}^2(r)g_{ij}(r) d^3r \quad (2.13)$$

ρ is the density. The distance dependence of the d - d hopping integrals is assumed to follow an exponential law $t_{ij}^0 \exp(-3(r - r_0)/r_0)$ [21], r_0 being the mean nearest neighbour distance and t_{ij}^0 being related to the bandwidths of the component. The electronic density of states $N(E, \sigma, \varepsilon, K)$ is given by:

$$N(E, \sigma, \varepsilon, K) = -\frac{1}{\pi} \lim_{\delta \rightarrow 0^+} |\text{Im}(x_A G_A(E + i\delta) + x_B G_B(E + i\delta))| \quad (2.14)$$

The strategy of the calculation is thus as follows: in order to calculate the electronic density of state $N(E, \sigma, \varepsilon, K)$ at arbitrary composition and arbitrary (σ, ε, K) parameters, we need only information about pure element properties which are the bandwidths W_A and W_B and the on site energies E_A and E_B . After computations of the local densities of states, charge transfers between the two elements are determined and the resulting Coulomb interaction incorporated into the total energy using equation (2.4). The calculation of the local density of states is iterated until relative changes in the charge transfers are less than 10^{-4} , at which electronic self-consistency has been achieved.

Table 1. Electronic tight-binding parameters of transition metals.

Element	d centre (eV)	d bandwidth (eV)	Nd
Ni	-4.9	3.8	9
Y	-1.8	6.6	2
Ti	-2.1	6.1	3
Zr	-2.2	7.7	3
Nb	-3.2	9.7	4

In principle, the parameters of the reference system, σ , ε and K , are thus determined by minimising, at a given temperature, the alloy free energy expression given in equation (2.7). The ordering energy is then simply equal to $E_T(\sigma, \varepsilon, K) - E_T(0, 0)$.

However, as the repulsive energy is not included in our calculation, we cannot minimise the free energy as a function of σ , the total energy becoming more negative without bound if σ decreased. Thus we choose to fix σ by assuming that a packing fraction of $\eta = 0.56$ is representative of the alloy just above the glass-transition temperature. This is the value suggested by the extrapolated values of the excess entropies of the pure metals and the assumption that the total hard-sphere volume does not change on alloying. In I it has been shown that this value of packing fractions fits the Ni-Ti and Ni-Zr alloys at all concentrations. Let us recall that in this approach, metallic glass has been considered as a supercooled liquid. It has been shown by Hafner and Pasturel [10] that apart from the form of the second peak of $S_{NN}(q)$ which is absent in the supercooled liquid, the result of the variational calculation was in good agreement with the partial structure factors of glasses calculated with a molecular dynamics quench technique.

3. Results

Before we present our results in detail, we discuss the origin of the input parameters used in our calculations. Using a tight-binding Hamiltonian and a real space method to calculate the electronic density of states gives the possibility to perform total energy calculations for complex situations like amorphous alloys but however requires a parametrisation of this situation. The tight-binding Hartree Hamiltonian that we have used includes both intersite and intrasite Coulomb interactions and incorporates the essential features required for a self-consistent treatment of charge transfer. The main tight-binding parameters are the on site and hopping energies.

For the intrinsic on site energies, which are the starting values for our self-consistent treatment of charge transfer, we have used atomic eigenvalues as suggested by Robbins and Falicov [22, 23]. These eigenvalues were calculated [22, 23] for a relativistic atom with one s electron and all d orbitals equally occupied, electronic configuration which is close to the $s^{1.3}d^{z-1.3}$ configuration predicted by band structure calculations [24].

The hopping integrals are obtained using a Slater-Koster parametrisation scheme [25]. The hopping energies between like species were evaluated from Harrison [21] who has fitted the bandwidths (W_i) of the pure metals predicted by Andersen and Jepsen [26]. The expression of the Slater-Koster parameter between unlike atoms can be derived using Shiba's approximation [27].

The last electronic input parameter is the intra-atomic Coulomb interaction. Theoretical estimates place its value between 2 and 3 eV [28]. In our calculations we have taken $U = 3$ eV for all the elements. Let us mention that another value of U in the given range does not change our results due to the self-consistent treatment of the charge transfer.

At this point of discussion it is important to recall that although the microscopic theory we use is not *ab initio*, it only requires the results of band structure calculations for the pure elements which are generally available [21, 24]. On the other side, such an approach has been already developed to study stability of compounds or solid solutions, using the same set of intrinsic tight-binding parameters [22, 23, 29, 32]. A good agreement between energies of formation of compounds or solid solutions and the experimental results [33] or results obtained from *ab initio* calculations [34] justifies *a posteriori* the use of this tight-binding parametrisation to obtain semi-quantitative results and we think that it can be extended to amorphous alloys without problem.

Concerning the other parameters, we have already discussed the value of the packing fraction. There remain the temperature T at which the free energy minimisation has been made and the density of alloy. The latter is obtained by a linear interpolation between the densities of the pure metals which has been confirmed by experiments of Altounian and Strom-Olsen [35]. For all alloys, the calculations have been performed at $T = 700$ K; this is within about 100 K of the glass temperature of these amorphous alloys [36].

To conclude this discussion, let us mention that these last parameters, σ , η , and T can be varied within a range of 15% without affecting the significant features of our results.

3.1. Ni_xZr_{1-x} alloys

We begin by studying Ni_xZr_{1-x} amorphous alloys which provide the opportunity to study the CSRO as a function of composition. Several accurate determinations of the partial structure factors using neutron and x-ray diffraction have been made in this system. Indeed CSRO has been found important for $Ni_{65}Zr_{35}$ alloy [4], weaker for $Ni_{50}Zr_{50}$ alloys [3], and practically zero for $Ni_{35}Zr_{65}$ alloys [2]. In I we have shown that the calculated partial structure factors $S_{cc}(q)$ are in good agreement with the experimental ones and were able to reproduce the strong evolution of $S_{cc}(q)$ as a function of composition. In this work, we focus our attention on the thermodynamic excess functions. In figure 1 we present the calculated ordering energies and ordering entropies for NiZr system. Once more the evolution of ordering energies and ordering entropies with respect to composition is very peculiar, these two quantities being maximum for $x_{Ni} = 0.7$.

Let us now look at the thermodynamic functions and more particularly the heats of formation, ΔH_f . From this point of view, the NiZr system is interesting since experimental determinations of the heats of formation have been performed for a number of Ni_xZr_{1-x} alloys [37]. In figure 2 we present our calculated heats of formation of amorphous alloys for the equilibrium ordered state and for the disordered state. The agreement between experimental and calculated results is very satisfying, especially when we take into account ordering energy. We can also conclude from the evolution of CSRO as a function of composition that the degree to which CSRO occurs will be the larger, the more negative the corresponding value of ΔH_f .

The second point is to compare these values to the ones of crystalline alloys. As can be seen from figure 2, amorphous alloys are characterised by formation enthalpies which

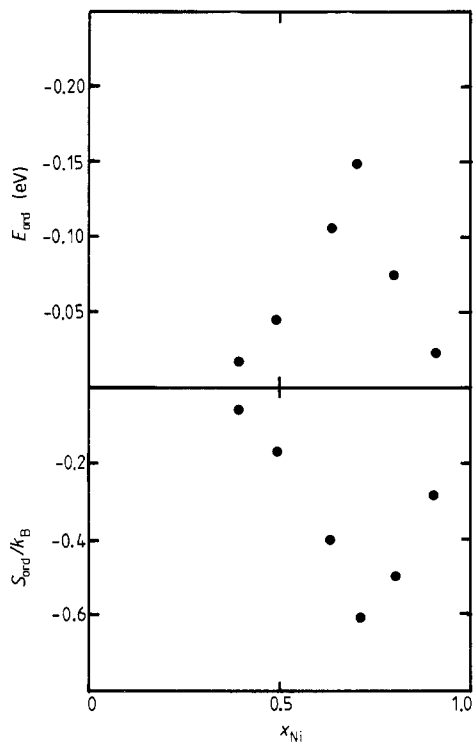


Figure 1. Ordering energies and ordering entropies of amorphous Ni_xZr_{1-x} alloys.

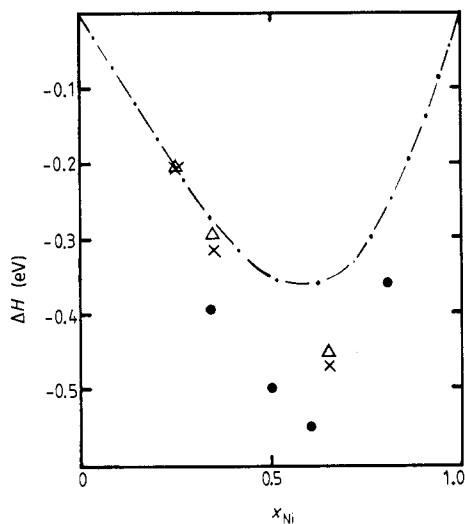


Figure 2. Calculated heats of formation in the NiZr system: —, without CSRO; Δ , with the equilibrium ordering energy; \times , experimental part; \bullet , experimental heats of formation of compounds.

adopt less negative values than those of crystalline alloys of similar composition (in fact, the difference between the two enthalpy terms is the crystallisation enthalpy ΔH_{cr} [37]). If CSRO occurs, amorphous alloys are stabilised since the absolute value of the ordering energy increases and consequently the enthalpy value found for the amorphous alloys tends to be close to the value expected for the crystalline material.

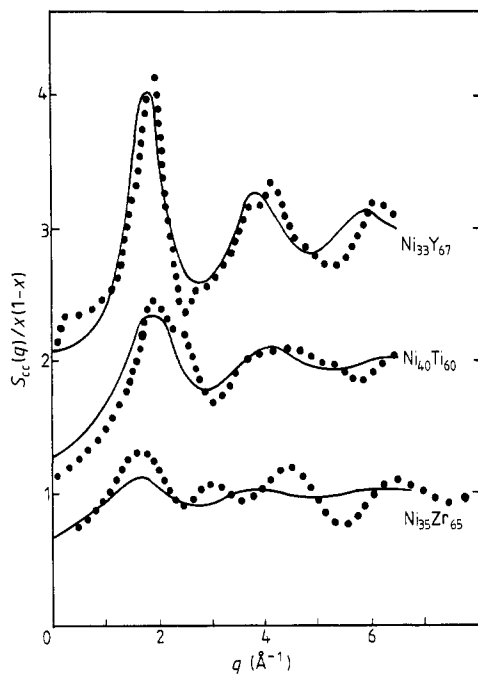


Figure 3. Evolution of the partial structure factors $S_{cc}(q)$ as a function of the alloying partner (\circ , experimental; —, calculated).

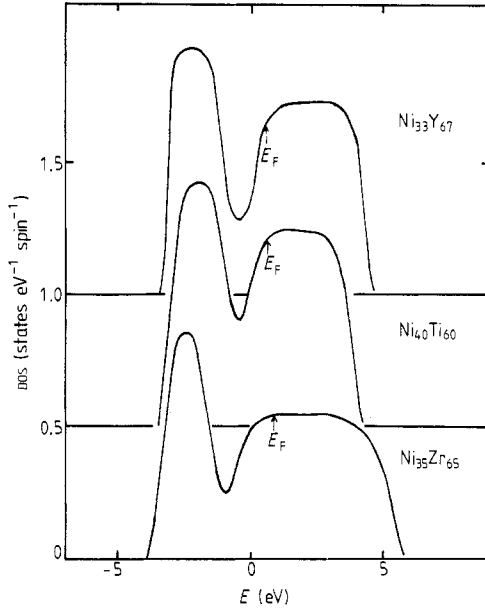
In the above discussion, we have implicitly admitted that a glassy alloy was formed but what are the consequences of CSRO on the metallic glass forming ability? As shown above, our model makes it possible to display the influence of electronic effects on the stabilisation of the disordered phase by the occurrence of CSRO or, in other words, by the occurrence of a strong chemical bonding between dissimilar atoms. However, our electronic factors, i.e. difference between the atomic energy levels of the d bands of the constituents, difference of their bandwidths and valence electron composition, are structure-alloy independent factors and our model points out the similarity of the chemical bonding in crystalline, amorphous and liquid alloys. The study of the NiZr phase diagram shows that stable compounds occur in the Ni rich side, in the region for which one finds a stronger CSRO parameter. Consequently, a tendency to short-range order in the liquid enhances the glass-forming ability only if this type of ordering is incompatible with any stable crystalline alloy.

3.2. Ni_xTM_{1-x} alloys

In this part, we have chosen to study the evolution of CSRO as a function of the alloying partner. We have performed CSRO calculations for $Ni_{40}Ti_{60}$, $Ni_{33}Y_{67}$ and $Ni_{40}Nb_{60}$ amorphous alloy [1] the $S_{cc}(q)$ partial structure factor has been derived from the combination of x-ray and neutron diffraction experiments. For $Ni_{33}Y_{67}$ and $Ni_{40}Nb_{60}$ amorphous alloys, the $S_{cc}(q)$ factors have been evaluated by neutron diffraction using isotopic substitution. These alloys have roughly the same composition than the one of $Ni_{35}Zr_{65}$ alloys and thus allow us to study the evolution of CSRO as a function of alloying partner. In figure 3, we can see that the variationally determined partial static structure factors compare well with those determined from isotope substitution experiments. In order to compare the chemical ordering in these different glasses, we report in table

Table 2. Ordering energies and Warren–Cowley parameters for $\text{Ni}_x\text{TM}_{1-x}$ alloys.

Alloy	ΔE_{ord} (eV)	σ_{WC}
$\text{Ni}_{33}\text{Y}_{67}$	-0.0176	-0.15
$\text{Ni}_{40}\text{Ti}_{60}$	-0.0126	-0.1
$\text{Ni}_{35}\text{Zr}_{65}$	-0.007	-0.05
$\text{Ni}_{40}\text{Nb}_{60}$	0	0

**Figure 4.** Evolution of the density of electronic states as a function of the alloying partner.

2 the calculated values of ordering energies and Warren–Cowley short range order parameter [38]. As seen in table 2, $\text{Ni}_{33}\text{Y}_{67}$ glass exhibits the strongest chemical ordering effect. When we compare the chemical interactions between Ni and other metals of the same column of the periodic table, it turns out that the tendency towards strong bonding interactions between Ni and d elements decreases going from 3d to 4d elements (see $\text{Ni}_{40}\text{Ti}_{60}$ and $\text{Ni}_{36}\text{Zr}_{65}$). Moreover, from the Warren Cowley parameters for $\text{Ni}_{33}\text{Y}_{67}$, $\text{Ni}_{36}\text{Zr}_{64}$ and $\text{Ni}_{40}\text{Nb}_{60}$, the chemical ordering also decreases as the MT element goes towards the right-hand side of the 4d row of the Periodic Table. In I a connection between the position of the Fermi level in the electronic densities of states of $\text{Ni}_x\text{Zr}_{1-x}$ alloys and the occurrence of CSRO has been proposed.

In figure 4 we present the densities of states of the $\text{Ni}_x\text{MT}_{1-x}$ alloys and its evolution as a function of the MT element. As for $\text{Ni}_{65}\text{Zr}_{35}$ alloy, we can see that $\text{Ni}_{33}\text{Y}_{67}$ alloy, which displays an important chemical ordering, is characterised by a Fermi level residing in a well-defined pseudogap. On the other hand, it is not the case for $\text{Ni}_{40}\text{Nb}_{60}$ alloy which has no chemical ordering. For this series of alloys, the same conclusion about the importance of the position of E_F is reached.

This general trend allows us to propose a discussion on the microscopic origin of CSRO in terms of elemental electronic characteristics (on site energy and bandwidth).

4. Discussion

The purpose of this section is to present a discussion of the microscopic origin of CSRO. We show that the variation of energy with the atomic positions can be decomposed into kinetic and ionic parts and we explain qualitatively their behaviour. Thus one can understand the main features of the results present above.

We recall that in our approach, we take only into account the variation of the bonding energy E_{bond} with CSRO (equation (2.8)). The energy of the fundamental electronic state contains two contributions:

$$E_T = \langle H_c \rangle + E_I(n_{i\mu}, \mathbf{r}_i) \quad (4.1)$$

$\langle H_c \rangle$ is the average value of the kinetic energy (second term in the right hand side of equation 2.10) and E_I is the average value of the Hamiltonian describing the orbital energy and the interaction between the charges of the system. $E_I(n_{i\mu}, \mathbf{r}_i)$ is a function of the charges $n_{i\mu}$ of the orbitals $|i\mu\rangle$ and of the positions \mathbf{r}_i of atoms i .

Within the Hartree approximation which is used here one has the one electron Hamiltonian (2.10)

$$H_{1e} = H_c + \sum_{i\mu} |i\mu\rangle \langle i\mu| \tilde{\epsilon}_{i\mu} \quad (4.2)$$

$\tilde{\epsilon}_{i\mu}$ is the energy of the atomic orbital $|i\mu\rangle$ renormalised by the interaction with electrons and ions. When charge transfers are self-consistent one has

$$\tilde{\epsilon}_{i\mu} = \frac{\partial E_I}{\partial n_{i\mu}} \quad (4.3)$$

where the partial derivative with respect to $n_{i\mu}$ indicates that the other variables $n_{j\mu}$ ($j\mu \neq i\mu$) and \mathbf{r}_i are constant. The total energy of the system can be written using (4.1) and (4.2)

$$E_T = \langle H_{1e} \rangle + E_I - \sum_{i\mu} n_{i\mu} \tilde{\epsilon}_{i\mu} \quad (4.4)$$

from (2.9), we see that

$$\langle H_{\text{ion-ion}} - H_{\text{c-e}} \rangle = E_I - \sum_{i\mu} n_{i\mu} \tilde{\epsilon}_{i\mu} \quad (4.5)$$

When the positions \mathbf{r}_i of the atoms vary (in the present study this is described by a variation of the Warren–Cowley parameter) the hopping integrals t_{ij} on H_c and the interaction between the charges of different atoms given by $V(r)$ (equation 2.11) vary. Thus the selfconsistent charges $n_{i\mu}$ and energy levels $\epsilon_{i\mu}$ vary also since the Hamiltonian is modified. In paper I, the variation of energy ΔE_T due to the occurrence of CSRO was decomposed in $\Delta \langle H_{1e} \rangle$ and $\Delta \langle H_{\text{ion-ion}} - H_{\text{c-e}} \rangle$. Here we use another decomposition in kinetic ΔE_1 and ionic ΔE_2 term which are more physical and easier to analyse as we show below.

In our definition ΔE_1 is the variation of the sum of one electron energies $\langle H_{1e} \rangle$ which one would obtain by taking into account the variation of the kinetic Hamiltonian H_c but not that of $\tilde{\epsilon}_{i\mu}$. This contribution is the only one considered by Bieber *et al* [8, 39] in binary substitutional transition metal alloys. More precisely we consider an intermediate state for the one electron tight-binding Hamiltonian H_{1e}^{int} with the kinetic part H_c equal

to that of the system with order, and the on site energy $\widetilde{\epsilon}_{i\mu}$ equal to that of the system without order.

$$\Delta\langle H_{1e}\rangle = \Delta_1\langle H_{1e}\rangle + \Delta_2\langle H_{1e}\rangle \quad (4.6)$$

$$\Delta E_1 = \Delta_1\langle H_{1e}\rangle \quad (4.7)$$

Δ_1 denotes the variation of the sum of one electron energy between the intermediate state and the state without order and Δ_2 denotes the variation between the state with order and the intermediate state.

$$\Delta_1\langle H_{1e}\rangle = -\langle H_{1e}(\sigma=0)\rangle_{\sigma=0} + \langle H_{1e}^{\text{int}}\rangle_{\text{int}} \quad (4.8a)$$

$$\Delta_2\langle H_{1e}\rangle = \langle H_{1e}^\sigma\rangle_\sigma - \langle H_{1e}^{\text{int}}\rangle_{\text{int}} \quad (4.8b)$$

ΔE_2 is defined as the difference $\Delta E_T - \Delta E_1$. The interesting point is that, with error of only second order in the variation of the selfconsistent charges $n_{i\mu}$ and orbital energies $\widetilde{\epsilon}_{i\mu}$, ΔE_2 has a simple expression. Indeed

$$\Delta E_2 = \Delta_2\langle H_{1e}\rangle + \Delta E_1 - \Delta\left(\sum_{i\mu} n_{i\mu} \widetilde{\epsilon}_{i\mu}\right). \quad (4.9)$$

Where $\Delta_2\langle H_{1e}\rangle$ is defined above. Using Hellmann–Feynman theorem one gets to first order in $d\widetilde{\epsilon}_{i\mu}$

$$\Delta_2\langle H_{1e}\rangle = \left\langle \sum_{i\mu} |i\mu\rangle \langle i\mu| d\widetilde{\epsilon}_{i\mu} \right\rangle = \sum_{i\mu} n_{i\mu} d\widetilde{\epsilon}_{i\mu} \quad (4.10)$$

In equation (4.7) the charges $n_{i\mu}$ are those calculated for the intermediate Hamiltonian and differ from those of the state without order by term of order $d\epsilon_{i\mu}$. Thus within error of order two in $d\widetilde{\epsilon}_{i\mu}$ we get

$$\Delta_2\langle H_{1e}\rangle = \sum_{i\mu} n_{i\mu} d\widetilde{\epsilon}_{i\mu}. \quad (4.11)$$

Where $n_{i\mu}$ is the charge calculated for the system without order.

Putting in (4.6) we obtain to first order in $d\widetilde{\epsilon}_{i\mu}$ and $dn_{i\mu}$

$$\Delta E_2 \approx \Delta E_1 - \sum_{i\mu} \widetilde{\epsilon}_{i\mu} dn_{i\mu} \approx \sum_i d\mathbf{r}_i \cdot \frac{\partial E_i}{\partial \mathbf{r}_i} \quad (4.12)$$

since $\epsilon_{i\mu}$ is given by (4.3).

Equation (4.12) shows that the variations of the selfconsistent charges $n_{i\mu}$ and energies $\widetilde{\epsilon}_{i\mu}$ cancel to first order. This is quite analogous to the local force theorem proved by Andersen [40] in the density functional formalism. We show below that the approximation given by (4.12) for ΔE_2 is always very good for the systems studied here.

Thus, to first order, ΔE_2 is the variation of the interaction energy obtained by moving the atoms with a fixed charge $n_{i\mu}$ on each orbital. We see that ΔE_2 is an ionic contribution to the variation of the total energy ΔE_T . Finally we note that in the GPM theory, developed by Gautier and coworkers, the kinetic contribution ΔE_1 is decomposed into a sum of pair interactions: this decomposition is also valid for ΔE_2 although this contribution is not taken into account in the GPM.

We have calculated the contributions ΔE_1 (kinetic) and ΔE_2 (as approximated by 4.12) for $\text{Ni}_{40}\text{Ti}_{60}$ and $\text{Ni}_x\text{Zr}_{1-x}$ ($x = 0.35, 0.5, 0.65$) in their equilibrium configuration.

Table 3. Ordering energy and its contribution for $\text{Ni}_{40}\text{Ti}_{60}$ and $\text{Ni}_x\text{Zr}_{1-x}$ alloys in their chemical equilibrium configuration.

	ΔE_{ord} (eV)	ΔE_1 (eV)	ΔE_2 (eV)	$\Delta\langle H_{1e} \rangle$ (eV)	$\Delta\langle H_{\text{ii}} - H_{\text{ee}} \rangle$ (eV)
$\text{Ni}_{40}\text{Ti}_{60}$	-0.0126	-0.0109	-0.0015	-0.0407	0.0281
$\text{Ni}_{35}\text{Zr}_{65}$	-0.0071	-0.0068	-0.0002	-0.0298	0.0227
$\text{Ni}_{50}\text{Zr}_{50}$	-0.0400	-0.0347	-0.0033	-0.0635	0.0235
$\text{Ni}_{65}\text{Zr}_{35}$	-0.115	-0.0972	-0.0118	-0.0151	-0.0999

Table 3 shows that, for $\text{Ni}_{40}\text{Ti}_{60}$, we make a very small error in approximating ΔE_2 by the formula (4.12) since the sum $\Delta E_1 + \Delta E_2$ is nearly equal to the exact ordering energy ΔE_{ord} . Calculations show that it is also true for the other alloys presented in this paper, and thus $\Delta E_2 = \Delta E_{\text{ord}} - \Delta E_1$ can be considered as the ionic contribution to the ordering energy given by (4.12). In table 3, we have also indicated the decomposition of ΔE_{ord} in $\Delta\langle H_{1e} \rangle$ and $\Delta\langle H_{\text{ion-ion}} - H_{\text{ee}} \rangle$. We see that both terms are important, as compared to ΔE_{ord} , but tend to cancel each other, contrary to ΔE_1 (kinetic) and ΔE_2 (ionic) which contribute with the same sign and are smaller than ΔE_{ord} .

If we compare ΔE_1 and ΔE_2 , we see that for $\text{Ni}_{40}\text{Ti}_{60}$ and $\text{Ni}_x\text{Zr}_{1-x}$, ΔE_1 is always the most important contribution to ΔE_{ord} . This is due to the fact that the charge transfer in the binary transition metals alloys is weak and thus the ionic contribution ΔE_2 is also weak (for instance, charge transfer on Ni atom is equal to 0.14 in $\text{Ni}_{40}\text{Ti}_{60}$ alloy).

Before analysing the behaviour of ΔE_1 and ΔE_2 , it is important to note that those terms vary roughly linearly with CSRO. This means that they would, alone, lead to a maximum CSRO. Thus one sees that the entropy is important in giving a partial CSRO for which its derivative compensates that of the energy.

The electrostatic energy of the charges carried by the atoms is the sum of two terms. The first one, positive, is due to the interaction between atoms of the same species and the second one, negative, is due to the interaction between atoms of different species. The CSRO diminishes the number of homoatomic nearest-neighbour pairs and increases the number of heteroatomic pairs, thus the ionic contribution ΔE_2 is the sum of two negative terms and always favours heteroatomic coordination.

However, we have seen from table 3 that ΔE_1 is the most important term and we discuss now its behaviour as a function of the band filling. In figure 5, we represent the evolution of ΔE_1 (calculated for Warren–Cowley parameter $\sigma_{\text{WC}} = -0.1$) as a function of the number of valence electrons, and for a DOS taken as the one of $\text{Ni}_{50}\text{Zr}_{50}$ amorphous alloy. The energy ΔE_1 has two zeros as a function of the band filling as it is well-known. Generally, this result is explained through an argument based on the moments of the DOS, but it can be also understood through the following physical argument. As already mentioned above, the calculated DOS of binary transition metals amorphous alloys is characterised by a two-peaked structure and in each peak the DOS is largely dominated by the contribution of one species since the mixing is weak between the two bands. The effect of CSRO is to diminish the number of homoatomic pairs and to increase the number of heteroatomic pairs. The consequences on the shape of the alloy DOS is that CSRO diminishes the bandwidths of the two subbands but increases their coupling which is important between the two peaks. Thus if the band filling is such that the Fermi level is in one of the two peaks of the DOS the ordered state is energetically unfavourable since the bandwidths are reduced. In contrast, if the Fermi level resides between the two

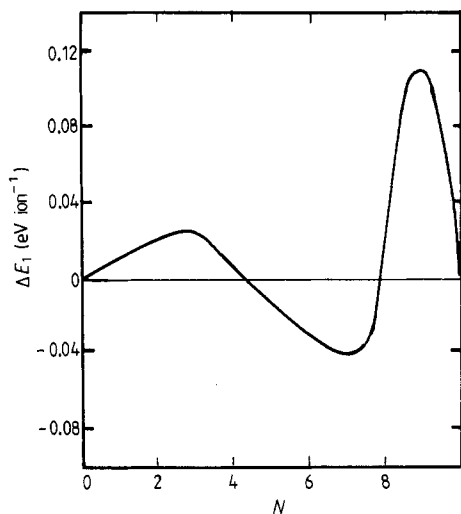


Figure 5. Evolution of the ordering energy as a function of the band filling.

peaks, the band energy is sensitive to the increase of the coupling between the two subbands and the CSRO is energetically more favourable.

We have understood why the occurrence of a pseudogap in the DOS and the location of the Fermi level in this pseudogap are necessary to obtain CSRO in amorphous transition metal alloys. The problem is now to know if an alloy does or does not develop a pseudogap in its density of states. In a tight-binding formalism, the occurrence of a pseudogap depends on the diagonal disorder, i.e. the difference between the centres of gravity of the d bands, and on the off-diagonal disorder, defined by the difference of the partners' bandwidths or the difference of the partners' d-d hopping integrals. Thus we have studied the variation of the ordering energy with the above two parameters. The evolution of ordering energy as a function of the increasing separation of the two bands is shown in figure 6(a) for the peculiar case of amorphous NiZr alloy; we start with the electronic tight-binding parameters of the alloy and only the separation of the d bands of the constituents, ΔE , is modified. We see that the ordering energy becomes more important when ΔE increases. In the same way, if we modify the off-diagonal disorder which is important for Ni₅₀Zr₅₀ alloy, a decreasing of this quantity tends to increase the ordering energy as it can be seen in figure 6(b). Thus from the electronic tight-binding parameters of table 1, we now understand qualitatively why CSRO is more important for Ni₄₀Ti₆₀ alloy than for Ni₃₆Zr₆₄ alloy, since the bandwidth of the early transition metal increases when we go down through a column; in the same way, if we enter a series, for instance from Y to Nb, CSRO diminishes because ΔE decreases.

5. Conclusion

We have presented calculations of CSRO in amorphous alloys of transition metals. Our method, based on a thermodynamic variational method, refers to thermodynamic equilibrium configurations but in agreement with earlier computer-simulation studies on simple metal alloys we find that calculations for the supercooled liquid phase yield useful information on the CSRO in the glassy phase.

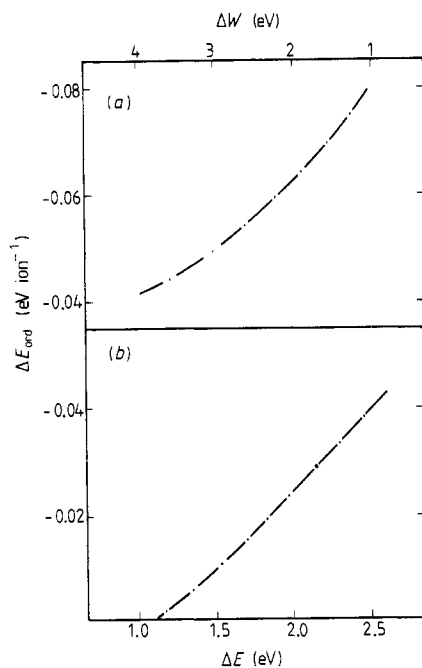


Figure 6. Evolution of the ordering energy as a function of (a) the difference of the partners' d-d hopping integrals and (b) the difference of the partners' d band centres.

We have shown that CSRO varies either with the composition for a given system, or with alloying partner for a given composition, in agreement with the experimental results. Using Hellmann–Feynman theorem, we show that the occurrence of CSRO results from two energy contributions; the first one is an electrostatic energy which always favours CSRO. In the studied alloys, it is weak due to a negligible charge transfer. The second contribution comes from the distortion of the electronic band with CSRO; the sign of this contribution depends crucially on the position of the Fermi level in the density of the electronic states. The CSRO is favoured by the occurrence of a pseudogap in the density of states and the location of the Fermi level in it. We have shown that the existence of the pseudogap can be correlated with the tight-binding parameters which are the difference between the d-band centres and the difference between the bandwidths. According to this analysis, we expect to find CSRO for transition metal alloys which respect at least the two following conditions: (i) the two alloying partners must be an early transition metal and a late transition metal-condition to obtain a pseudogap in the density of electronic states (let us mention that it is also a condition to obtain amorphous alloys by quenching method); (ii) the alloying composition must be rich in late transition metal condition to obtain the Fermi level in the pseudogap.

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$$\sigma_{WC} = \int_0^{r_M} g_{cc}(r) 4\pi r^2 dr / \int_0^{r_M} g_{NN}(r) 4\pi r^2 dr$$

r_M is the radial distance corresponding to the first minimum of $g_{NN}(r)$

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